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# PHOTOPOLYMERIZABLE COMPOSITION
[Hikari jugosei soseibutsu]

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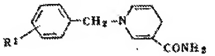
## Claim /1*

1. A photopolymerizable composition having as essential constituents (1) a polymerizable compound having at least 1 ethylenic unsaturated double bond, and (2) a photopolymerization initiator, characterized by the fact, that the photopolymerization initiator comprises: (a) at least one member selected from the group comprising a compound having at least 1 oxo-oxygen atom bound to an aromatic ring, and a compound having at least one oxo-oxygen atom bound to a carbon atom bound to a carbon atom of an aromatic ring; and (b) a 1-(unsubstituted or substituted) benzyl-1,4-dihydronicotinamide expressed by General Formula (I).



(I)

(In the formula, $R^1$ represents a halogen atom or an alkyl group of 1 to 5 carbon atoms.)

## Detailed explanation of the invention

### Industrial application field

The present invention pertains to a photopolymerizable composition; more specifically, it relates to a photopolymerizable composition that has the characteristics of a photopolymerization initiator.

### Prior art

Conventionally, it has been widely known that an unsaturated compound that is curable by radiation may be used as a component of compositions for paint, printing ink, and adhesives, for example. The aforementioned compound in a composition is polymerized and cured by the utilization of visible light, ultraviolet light, x-rays or other electromagnetic radiation, or by electron rays, neutron rays, alpha rays

* [Numbers in right margin indicate pagination of the original text.]

or other particle rays, and the rate of polymerization is remarkably increased when this action is brought about in the presence of a polymerization initiation compound. These technologies are disclosed in U.S. Patent Nos. 3,551,235, 3,551,246, 3,551,311 and 3,558,387, Belgian Patent No. 808,179, and Japanese Kokai Patent Application No. Sho 49[1974] 110781. These technologies produce superior flexibility, chemical resistance, anti-abrasion property, gloss, adhesion and hue; but on the other hand the composition curing sensitivity is low, so image formation requires a long exposure time. In the case of a detailed image, a slight vibration during the [exposure] operation [results] in the inability to reproduce /2
a good quality image. Alternatively [as a way of compensating for low sensitivity], the energy radiation value of the light source or particle-ray source may be increased for exposure, which makes it necessary to consider how the resulting great heat must be dissipated, and there are further problems with the deformation and quality degradation of the film due to heat.

[0003]

The inventors have conducted a series of diligent investigations in order to solve the problems described above by increasing the sensitivity of a photopolymerizable composition, and have discovered that it is possible to significantly increase the rate of photopolymerization of a polymerizable compound when a photopolymerization initiator of a predetermined composition has an ethylenic unsaturated double bond; thus arriving at the present invention.

[0004]

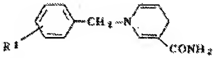
An object of the present invention is to offer a photopolymerization initiator and a photopolymerization initiator system of high sensitivity to be utilized in a photopolymerizable composition (one type of a so-called photosensitive resin (photopolymer)).

[0005]

A further object of the present invention is to offer a photopolymerization initiator and a photopolymerization initiator system with an increased rate of photopolymerization of a photopolymerizable composition that contains a polymerizable compound that has an ethylenic unsaturated double bond, widely and in general.

[0006]

The present invention is a photopolymerizable composition having as essential constituents (1) a polymerizable compound having at least 1 ethylenic unsaturated double bond, and (2) a photopolymerization initiator, characterized by the fact that the photopolymerization initiator comprises: (a) at least one member selected from the group comprising a compound having at least 1 oxo-oxygen atom bound to an aromatic ring, and a compound having at least one oxo-oxygen atom bound to a carbon atom of an aromatic ring; and (b) a 1-(unsubstituted or substituted)benzyl-1,4-dihydronicotinamide expressed by General Formula (I).



(I)

(In the formula, $R^1$ represents a halogen atom or an alkyl group of 1 to 5 carbon atoms.)

[0007]

The polymerizable compound in the photopolymerizable composition of this invention is a compound having at least one ethylenic unsaturated double bond (hereinunder called an ethylenic compound). It may be in the chemical form of a monomer, a prepolymer such as a dimer or trimer, and

other oligomers, and a mixture thereof, and a copolymer thereof. Examples include unsaturated carboxylic acids and salts thereof, aliphatic polyols thereof, oligoesters (and polyesters) having a hydroxyl group in the molecule, and esters with polyhydric phenols. (A polyol compound includes oligomers and polymers of oligoesters and polyesters with dibasic acids with the aforementioned polyol compound).

[0008]

Specific examples of an unsaturated carboxylic acid include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, and maleic acid. The salts of the unsaturated carboxylic acid include the aforementioned sodium salts and potassium salts.

[0009]

Examples of the aforementioned aliphatic polyol compound and polyhydric phenol include ethylene glycol, triethylene glycol, tetraethylene glycol, tetramethylene glycol, neopentyl glycol, 1,10-decanediol, 1,2-butanediol, 1,3-butanediol, propylene diol, propylene glycol, and other dihydric alcohols; trimethylol ethane, trimethylol propane, and other trihydric alcohols; as well as polymers thereof; pentaerythritol, dipentaerythritol, tripentaerythritol, and other polymeric pentaerythritols; sorbitol, d-mannitol and other sugars; dihydroxymaleic acid and other dihydroxy carboxylic acids; hydroquinone, resorcin, catechol, pyrogallol, and other polyhydric phenols. Specific examples of esters of the /3
aliphatic polyol compound and unsaturated carboxylic acid include acrylate esters such as ethylene glycol ester of diacrylic acid, triethylene glycol ester of triacrylic acid, 1,3-butane diol ester of diacrylic acid, tetramethylene glycol ester of diacrylic acid, propylene glycol ester of diacrylic acid, trimethylol propane ester of triacrylic acid, trimethylol ethane ester of triacrylic acid, tetraethylene glycol ester of

diacrylic acid, pentaerythritol ester of diacrylic acid, pentaerythritol ester of triacrylic acid, pentaerythritol ester of tetraacrylic acid, dipentaerythritol ester of diacrylic acid, dipentaerythritol ester of triacrylic acid, dipentaerythritol ester of tetraacrylic acid, dipentaerythritol ester of pentaacrylic acid, dipentaerythritol ester of hexaacrylic acid, tripentaerythritol ester of octaacrylic acid, dipentaerythritol ester of tetraacrylic acid [sic], dipentaerythritol ester of pentaacrylic acid [sic], dipentaerythritol ester of hexaacrylic acid [sic], tripentaerythritol ester of octaacrylic acid [sic], sorbitol ester of tricrylic acid, sorbitol ester of tetracrylic acid, sorbitol ester of pentacrylic acid, sorbitol ester of hexacrylic acid, and polyester acrylate oligomer, for example. Specific examples of a methacrylate ester include tetramethylene glycol ester of dimethacrylic acid, triethylene glycol ester of dimethacrylic acid, trimethylol propane ester of trimethacrylic acid, trimethylol ethane ester of trimethacrylic acid, pentaerythritol ester of dimethacrylic acid, pentaerythritol ester of trimethacrylic acid, dipentaerythritol ester of dimethacrylic acid, dipentaerythritol ester of dimethacrylic acid, pentaerythritol ester of dimethacrylic acid, pentaerythritol ester of trimethacrylic acid, dipentaerythritol ester of dimethacrylic acid [sic], dipentaerythritol ester of tetramethacrylic acid, tripentaerythritol ester of octamethacrylic acid, ethylene glycol ester of dimethacrylic acid, 1,3-butanediol ester of dimethacrylic acid, tetramethylene glycol ester of dimethacrylic acid, and sorbitol ester of tetramethacrylic acid. Specific examples of an itaconic acid ester include ethylene glycol ester of ditaconic acid, propylene glycol ester of diitaconic acid, 1,3-butanediol ester of diitaconic acid, 1,4-butanediol ester of diitaconic acid, tetramethylene glycol ester of diitaconic acid, pentaerythritol ester of diitaconic acid, dipentaerythritol ester of triitaconic acid, dipentaerythritol ester of pentaitaconic acid, dipentaerythritol ester of hexaitaconic acid, and sorbitol ester of tetraitaconic acid. Specific examples of crotonic acid esters include ethylene glycol ester of dicrotonic acid, propylene glycol ester of dicrotonic acid, tetramethylene glycol ester of dicrotonic acid, pentaerythritol ester of dicrotonic acid, and sorbitol ester of tetracrotonic acid. Specific

examples of isocrotonic acid esters include ethylene glycol ester of diisocrotonic acid, pentaerythritol ester of diisocrotonic acid, and sorbitol ester of tetraisocrotonic acid. Specific examples of maleic acid esters include ethylene glycol ester of dimaleic acid, triethylene glycol ester of dimaleic acid, pentaerythritol ester of dimaleic acid, and sorbitol ester of tetramaleic acid. Mixtures of the aforementioned esters can also be used.

[0010]

Oligoesters (or polyesters) having a hydroxyl group in the molecule, and unsaturated carboxylic acid esters are oligoester acrylates and oligoester methacryclates (hereinunder collectively called oligoester (meth)acrylates). An oligoester (meth)acrylate is a reaction product obtained by an esterification reaction of an acrylic acid or methacrylic acid, a polyhydric carboxylic acid, and a polyol, and is a /4
compound expressed by the hypothesized structural formula of General Formula (I)

$$(CH_2=\overset{R^2}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O)_n X \qquad (I)$$

Here $R^2$ represents a hydrogen atom or methyl group, X represents an ester residue containing at least 1 ester bond comprising polyol and polyhydric carboxylic acid, and *n* is an integer from 1 to 6.

[0011]

The polyol contained in the ester residue X may be a polyol such as ethylene glycol, 1,2-propylene glycol, 1,4-butane diol, 1,6-hexane diol, triemethylol propane, trimethylol ethane, 1,2,6-hexane triol, glycerine, pentaerythritol, or sorbitol, for example; or diethylene glycol, triethylene glycol, tetraethylene glycol, decaethylene glycol, tetradeca[e]thylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, or polypropylene glycol or similar polyether type, for example.

[0012]

Specific examples of a polyhydric carboxylic acid contained in ester residue X include phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, trimellitic acid, pyromellitic acid, benzophenone dicarboxylic acid, resorcinol diacetic acid, biphenol A diacetic acid and other aromatic polyhydric carboxylic acid; maleic acid, fumaric acid, himic acid, itaconic acid and other unsaturated aliphatic polyhydric carboxylic acids; malonic acid, succinic acid, glutaric acid adipic acid, pimelic acid, sebacic acid, dodecanoic acid, tetrahydrophthalic acid, and other saturated aliphatic polyhydric carboxylic acids, and the like.

[0013]

The ester leaving group X includes compounds that are structured from 1 type each of a polyol and a polyhydric alcohol as mentioned above, and compounds that are structured from 1 or the other of these, or from 2 or more types of these. It also includes compounds that contain 1 molecule each of polyol and polyhydric carboxylic acid in an ester leaving group X, and compounds that contain 1 of these or 2 molecules of both or more. Namely, it is possible to use any compound as long as at least 1 ester bond is contained in X. Also included are compounds in which a hydroxyl group remains in X, or where this forms an ester with a monovalent carboxylic acid, or where this is substituted by an alkoxy group such as methoxy or ethoxy, for example. It is also possible for carboxylic acid to remain in X. Ordinarily, the number $n$ in General Formula (II) and the number of ester bonds contained in X will be in the range of 1-6. When the value of $n$ is 2 or greater, it is possible to use a compound that contain only an acryloyl group or a methacryloyl group, but not both, in one polyester(meth)acrylate molecule; alternatively it is possible to use a compound that contains any proportion of acryloyl groups and methacryloyl groups in

one molecule. Specific examples and hypothetical structural formulae of an oligoester (meth)acrylate include the species of polyhydric alcohols and polybasic acids with an ester leaving group structure, as well as the compound disclosed as a polyester (meth)acrylate in the specification of Japanese Kokai Patent Application No. Sho 51-77324, with a number of *n* polymerizable functional groups on a molecule. It is also possible to mention the unsaturated esters disclosed in the specifications of Kokai Patent Application No. Sho 47-9676 (which corresponds to U.S. Patent 3,732,107).

[0014]

Next an explanation is given of the photopolymerization initiator that has a remarkable characteristic for the invented photopolymerizable composition. It is possible to use an aromatic acyloin, aromatic acyloin ether, aromatic ketone, and polycyclic quinones as the group comprising the compound having at least one oxo-oxygen atom bound to a carbon atom of an aromatic ring and a compound having at least 1 oxo-oxygen atom bound to the aromatic ring as Component (a) (hereinunder called an aromatic-series carbonyl compound). Specific examples of an aromatic acyloin include benzoin, o-toluoin, p-toluoin, and furoin. Specific examples of an aromatic acyloin ether include benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin sec-butyl ether, o-toluoin methyl ether, and p-toluoin methyl ether. Specific examples of an aromatic ketone include benzophenone, phenyl tolyl /5
ketone, 2-chlorobenzophenone, 2-chloroacetophenone, acetophenone, propiophenone, benzil, 2,2'-dimethylbenzil, Michler's ketone, bis(p-aminophenyl)ketone, phenyl β-naphthylketone, fluorenone, anthrone, benzanthrone, 10,10'-bianthrone, benzophenone oxide (xanthone), and benzophenone sulfide (thioxanthone). Specific examples of the polynuclear condensed quinones include anthraquinone, 1-hydroxyanthraquinone, 1-methylanthraquinone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone, 1-chloroanthraquinone, 1-bromoanthraquinone, 2-chloroanthraquinone,

phenanthraquinone, 1-methylphenanthraquinone, 4-ethylphenanthraquinone, 2-chlorophenanthraquinone, 3-bromophenanthraquinone, 2,7-dimethylphenanthraquinone, 2,7-di-tert-butylphenanthraquinone, and 1,2-benzanthraquinone.

[0015]

Of these aromatic carboxylic acids, benzanthrone, 1,2-benzanthroquinone, and fluorenone are preferred in terms of maximal photosensitivity, their availability, their stability over time and compatibility with photopolymerizable compositions, and the fastness of the formed image, for example.

[0016]

The component (b) of the photopolymerization initiator is an 1-(unsubstituted or substituted)benzyl-1,4-dihydronicotinamide expressed by General Formula (I). In General Formula (I), the substituent group R indicates a halogen atom such as a fluorine atom, chlorine atom, bromine atom, or iodine atom, or a hydrogen atom or an alkyl group of 1-3 carbon atoms such as a methyl, ethyl, propyl, or isopropyl group. In addition to the substituent group R, the benzyl group of the compound expressed by General Formula (I) may have a substitutent group $R^0$ (the specific examples are identical to those for R).

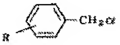
[0017]

Specific examples of the compound expressed by General Formula (I) include
1-benzyl-1,4-dihydronicotinamide (boiling point 122-124°C),
1-(4-chlorobenzyl)-1,4-dihydronicotinamide (boiling point 130-131°C),
1-(2-chlorobenzyl)-1,4-dihydronicotinamide (boiling point 139-141°C),

1-(2,4-dichlorobenzyl)-1,4-dihydronicotinamide, 1-(4-bromobenzyl)-1,4-dihydronicotinamide, 1-(2-methylbenzyl)-1,4-dihydronicotinamide (CAS Registry No. [56133-31-4]), 1-(4-methylbenzyl)-1,4-dihydronicotinamide (CAS Registry No. [56133-29-0]), 1-(4-ethylbenzyl)-1,4-dihydronicotinamide (boiling point 117-119°C), 1-(4-propylbenzyl) -1,4-dihydronicotinamide (boiling point 132-134°C), 1-(4-butylbenzyl)-1,4-dihydronicotinamide, 1-(4-pentylbenzyl)-1,4-dihydronicotinamide, 1-(4-isopropylbenzyl)-1,4-dihydronicotinamide, and 1-(4-isoamylbenzyl)-1,4-dihydronicotinamide.

[0018]

[With regards to the method for synthesis], the 1-(unsubstituted or substituted) benzyl-1,4-dihydronicotinamide expressed in General Formula (I) may be synthesized from the (unsubstituted or substituted)benzyl chloride expressed by General Formula (II) and nicotinamide according to the method described by Kurisu, Nakajima, and Okawara on page 160 and following in Kogyo Kagaku Zasshi [Journal of the Chemical Society of Japan, Industrial Chemistry Section], Vol. 71 (1968);




II

(R has the same meaning as the previously discussed R.)

according to the method described by J. F. Biellman and H. J. Callot in the Bull. Soc. Chim. Fr. Vol. 3 (1968), pages 1154-1159; or according to the method described by D. Mauzerall and F. H. Westheimer in J. Am. Chem. Soc., Vol. 77 (1955), pages 2261-2264. /6

[0019]

The amount of photopolymerization initiator contained in the invented photopolymerizable composition may vary over a wide range from approximately 0.01% to approximately 20% by weight with reference to the ethylene-type compound, preferably from approximately 0.1% to approximately 10%. The ratio (a):(b) of components of the photopolymerization initiator may vary in the range of approximately 30:1 to approximately 1:30, preferably approximately 10:1 to approximately 1:10.

[0020]

As the occasion may require, the photopolymerizable composition of this invention which contains the above-mentioned ethylenic compound and photopolymerization initiator may further contain known additives such as a binder, a heat-polymerization inhibitor, a plasticizer, a coloring agent, and a surface smoothing agent.

[0021]

The photopolymerizable composition may be combined with a film-forming polymeric substance (binder) for the purpose of forming a resist (thick) image on the photosensitive material, particularly for a photosensitive material that undergoes liquid development or a photosensitive material that undergoes peel-off development, to be described below. There are no particular limitations on the substance that is used as a binder, as long as it is an organic high-molecular weight polymer which is miscible with the polymerizable compound having an ethylenic unsaturated double bond. Preferred high-molecular weight polymers are those which permit peel-off development or development with water or weak alkaline aqueous solution. The organic high-molecular weight polymer should not only be [selected for use] as a film-forming agent for said composition, but should also be selected for its affinity, according to

whether the developer used is water, a weak alkaline aqueous solution, or a type of organic solvent. For example, the use of a water-soluble organic polymer will permit the development with water. Examples of such an organic high-molecular weight polymer include addition polymers having a carboxyl group in the side chain such as methacrylic acid copolymers, acrylic acid copolymers, itaconic acid copolymers, partially esterified maleic acid copolymers, maleic acid copolymers, and crotonic acid copolymers; similar [examples include] acid cellulose derivatives having a carboxyl group in the side chain. Addition polymers having a hydroxyl group obtained by addition of cyclic acid anhydride are also useful. Polyvinylpyrrolidone and polyethylene oxide are also useful as water-soluble organic high-molecular weight polymers. Moreover, alcohol-soluble nylon and a polyether composed of 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin are useful to strengthen that part of the film which has been cured after exposure. The above-mentioned organic high molecular weight polymer may be added in any amount, but favorable results in terms of the strength of the formed image are not obtained if the amount exceeds 90 wt%. Examples of a linear organic high molecular weight polymer used for peel-off development include homopolymers and co-polymers such as chlorinated polyolefins (with a chlorine content of approximately 60% to approximately 85% by weight) such as chlorinated polyethylene and chlorinated polypropylene; polymethyl methacrylate, polyacrylic acid, polymethacrylic acid; polyalkyl acrylate esters having methyl, ethyl, or butyl, as the alkyl group, for example; copolymers of alkyl acrylate ester (same alkyl as above) and at least one monomer of acrylonitrile, vinyl chloride, vinylidene chloride, styrene, and butadiene; polyvinyl chloride, vinyl chloride-acrylonitrile copolymer, polyvinylidene chloride, vinylidene chloride-acrylonitrile copolymer, polyvinyl acetate, vinyl acetate-vinyl chloride copolymer, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylonitrile, acrylonitrile-styrene copolymer, acrylonitrile-butadiene-styrene copolymer, polyvinyl alkyl ether (alkyl: methyl, ethyl, isopropyl, butyl, and the like), polymethyl vinyl ketone, polyethyl vinyl

ketone, polyethylene, polypropylene, polybutylene, polystyrene, poly-α-methylstyrene, polyamide (6-nylon, 6,6-nylon, and the like), poly-1,3-butadiene, polyisoprene, polyurethane, polyethylene terephthalate, polyethylene isophthalate, chlorinated rubber, polychloroprene, chlorinated rubber [sic], ethylcellulose, acetylcellulose, polyvinyl butyral, polyvinyl formal, styrene-butadiene rubber, and poly(chlorosulfonated ethylene). In the case that [the organic high molecular weight polymer] is a co-polymer, the ratio of the contained component monomers may vary over a wide range of values, /7 but generally the minority monomer ingredient should preferably be 10 to 50% by molar ratio. Thermoplastic polymeric substances other than those mentioned above may be used in the present invention, so long as they satisfy the above-mentioned conditions.

[0022]

Of the aforementioned polymers, those that are preferred for use with the invented photopolymerizable composition are polyethylene chloride (with a chloride content of approximately 60% to approximately 75% by weight), polypropylene chloride (with a chloride content of approximately 60% to approximately 75% by weight), polymethyl methacrylate, polyvinyl chloride, vinyl chloride-vinylidene chloride copolymer (a molar content of vinyl chloride of 20% to 80%), vinylidene chloride-acrylonitrile copolymer (a molar content of acrylonitrile of 10-30%), vinyl chloride-acrylonitrile copolymer (a molar content of acrylonitrile of 10-30%), polystyrene, polyvinyl butyral, polyvinyl acetate, polyvinyl formal, ethyl cellulose, acetyl cellulose, vinyl chloride-vinyl acetate copolymer, polychloroprene, polyisoprene, chlorinated rubber, and chlorosulfonated polyethylene, for example.

[0023]

These polymers may be used alone, but it is also possible to use a mixture of two or more types, in a suitable ratio, of polymers with good [miscibility] to a degree that demixing does not occur during [any step] of the manufacturing process from the preparation of the solution (coating solution) of the photopolymerizable composition through the coating and drying [steps].

[0024]

Specific examples of a thermal polymerization inhibitor which can be used include para-methoxy phenol, hydroquinone, alkyl- or aryl-substituted hydroquinone, t-butyl catechol, pyrogallol, cuprous chloride, phenothiazine, chloranil, naphthylamine, β-naphthol, 2,6-di-t-butyl-p-cresol, pyridine, nitrobenzene, dinitrobenzene, p-toluidine, Methyl Blue, and organic acid-copper compounds (for example, copper acetate). The amount of the thermal polymerization inhibitor added is preferably from 0.001 to 5 parts by weight per 100 parts by weight of the above-described ethylenic compound. The thermal polymerization inhibitor can be added for the purpose of increasing the stability over time prior to light exposure of the photopolymerizable composition of the invention.

[0025]

Specific examples of a colorant include titanium oxide, carbon black, iron oxide, phthalocyanine-type pigments, azo-type pigments and other pigments, methylene blue, crystal violet, rhodamine B, fuchsin, auramin, azo-type dyes, anthraquinone-type dyes, and other dyes; it is preferred that a colorant that does not absorb light of the wavelength of the photopolymerization initiator be used as the colorant. The colorant may be added preferably in an amount of from 0.1 to 30 parts by weight in the case of a pigment, or 0.01 to 10 parts by weight in the case of a dye preferably from 0.1 to 3 parts by weight, per

100 parts by weight of the total amount of binder and ethylenic compound. In the case that the above-mentioned coloring agent is used, it is preferably to add an adjuvant substance such as dichloromethyl stearate and other chlorinated fatty acid, in the range of 0.005 to 0.5 parts by weight per 1 part by weight of coloring agent. An adjuvant substance for a coloring agent is not required when the photopolymerizable composition contains a plasticizer. Examples of the plasticizer include phthalic esters such as dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diisobutyl phthalate, dioctyl phthalate, octyl capryl phthalate, dicyclohexyl phthalate, ditridecyl phthalate, butylbenzyl phthalate, diisodecyl phthalate, and diallyl phthalate; glycol esters such as dimethyl glycol phthalate, ethyl phthalyl ethyl glycolate, methylphthalyl ethyl glycolate, butyl phthalyl butyl glycolate, and triethylene glycol dicaprylate esters; phosphoric esters such as tricresyl phosphate and triphenyl phosphate; esters of aliphatic dibasic acids such as diisobutyl adipate, dioctyl adipate, dimethyl sebacate, dibutyl sebacate, dioctyl acylate, and dibutyl maleate; and triethyl citrate, glycerol triacetyl ester, and butyl laurate.

[0026] /8

Examples of a surface smoothing agents include lanolin, paraffin wax, and natural wax.

[0027]

As the occasion may require, the above-mentioned modifiers may be added in an amount up to 3% by weight, and preferably up to 1% by weight, based on the total weight of the photopolymerizable composition of this invention.

[0028]

The most general method for utilizing the invented photopolymerizable composition is for the invented photopolymerizable composition to be dissolved in a solvent, and the [resulting] solution (solution of photopolymerizable composition) to be applied to a substrate according to the conventional method, and after the solvent is removed, it is used as a photopolymerizable photosensitive material.

[0029]

Examples of the solvent include acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, diisobutyl ketone, and other ketones; ethyl acetate, butyl acetate, amyl acetate, methyl formate, ethyl propionate, dimethyl phthalate, ethyl benzoate, and other esters; toluene, xylene, benzene, ethyl benzene, and other aromatic hydrocarbons; carbon tetrachloride, trichloroethylene, chloroform, 1,1,1-trichloroethane, monochlorobenzene, chloronaphthalene, and other halogenated hydrocarbons; tetrahydrofuran, diethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether acetate, and other ethers; and dimethylformamide and dimethyl sulfoxide.

[0030]

The substrate to which the invented photopolymerizable composition is applied in a suitable form (for example, as the aforementioned solution form) is preferably a substrate having a flat shape or other shape that is not subject to dimensional instability. Examples of flat substrates include [plates or sheets or laminates of] glass, silicon oxide, ceramics, paper, metals such as aluminum, zinc, magnesium, copper, iron, chromium, nickel, silver, gold, platinum, palladium, aluminum base alloys, zinc base alloys, magnesium base alloys, copper-zinc alloys, iron-nickel-chromium alloys, and copper base alloys; metal compounds such as aluminum oxide, tin oxide ($SnO_2$) and indium oxide ($In_2O_3$); polymers such as

regenerated cellulose, cellulose nitrate, cellulose diacetate, cellulose triacetate, cellulose acetate butyrate, cellulose acetate propionate, polystyrene, polyethylene terephthalate, polyethylene isophthalate, polycarbonate of bisphenol A, polyethylene, polypropylene, nylons (6-nylon, 6,6-nylon, and 6,10-nylon, for example), polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, vinyl chloride-acrylonitrile copolymer, vinyl chloride-vinylidene chloride copolymer, polyacrylonitrile, methyl polyacrylate, and methyl polymethacrylate. The above-mentioned flat substrates may be used in the form of a laminate which is prepared by firmly adhering at least two thin plates as described above, such as cermet, iron-aluminum laminate, iron-copper-aluminum laminate, iron-chromium-copper laminate, polyethylene-coated paper, cellulose triacetate-coated paper, anodized aluminum plate having a surface layer of aluminum oxide, chromium plate having a surface layer of chromium oxide formed by methods known in the art, glass plate having a surface layer of tin oxide, and silicon oxide plate having a surface layer of indium oxide.

[0031]

The substrate may be transparent or opaque depending on the intended use of the photosensitive image-forming material. In addition to the case of a transparent substrate or the case of an opaque substrate, it is possible to use a colored transparent substrate, that has been colored by addition of a dye or pigment as described in the J. SMPTE [Journal of the Society of Motion Picture and Television Engineers], Vol. 67, p. 296 (1958). The opaque substrate may be made of paper or metal which is inherently opaque or made of any transparent material to which a dye or pigment such as titanium oxide has been added. It is also possible to use a plastic film which has undergone surface treatment according to the method described in Japanese Patent Publication No. 19068, as well as paper and plastic films which are made completely opaque by the addition of carbon black and the like. The substrate may be

treated so as to have minute irregularities, by sanding, electrolytic etching, anodization, or chemical etching, for example. It is also possible to use a substrate that has been subjected to a surface treatment such as corona discharge, UV light irradiation, and flame treatment, for example. It is also possible to /9
use a plastic substrate that has been reinforced by the admixture of a reinforcing substance such as glass fibers, carbon fibers, boron fibers, various metal fibers, metal wiskers, and the like.

[0032]

As the occasion may require, the surface of the substrate may be provided with a primer coat, anti-halation coating, UV absorbing layer, or visible light absorbing layer.

[0033]

In order to prevent the invented composition from decreasing in sensitivity on account of oxygen, exposure is performed using a vacuum printing frame [placed on the photosensitive layer] as disclosed in U.S. Patent No. 3,060,026, or with a removable transparent cover [placed on the photosensitive layer], or with an oxygen-impervious coating layer placed on the photosensitive layer as disclosed in Japanese Patent No. Sho 40[1985]-17828.

[0034]

The factors that determine the rate of photopolymerization/curing and drying of the invented photopolymerizable composition include such things as the substrate, and particularly the surface properties of the substrate, the specific ingredients in the composition, the amount of photopolymerization initiator in the entire photopolymerizable composition, the thickness of the photopolymerizable composition layer, the properties (particularly the irradiated spectrum) of the light

source, the intensity of light, the presence or absence of oxygen, and the ambient temperature. The exposure may be carried out by any of various methods used individually or in combination. For example the composition may be exposed to active light rays obtained by any type of light source, so long as an effective exposure is obtained; the reason being that the invented photopolymerizable composition generally shows maximum sensitivity in the spectral range from ultraviolet light to visible light, or from about 180 nm to 600 nm in wavelength. Because the invented composition is also sensitive to electromagnetic waves of short wavelengths such as vacuum ultraviolet rays, x-rays, and gamma-rays, as well as particle rays such as electron rays, neutron rays, and alpha-rays, these types of radiation can also be utilized for image exposure. Examples of suitable light sources for ultraviolet light and visible light include a carbon arc lamp, mercury vapor lamp, xenon lamp, fluorescent lamp, argon glow discharge lamp, photographic flood lamp, and Van de Graaff accelerator.

[0035]

The irradiation period must be long enough to provide an effective exposure. The irradiation may be carried out at any temperature, but room temperature, namely, the range of 10°C to 40°C, is preferred for practical reasons. When cured by light, the invented composition becomes a dry, resilient material which is resistant to wear and chemicals, and exhibits good ink receptivity, hydrophilic-hydrophobic balance, anti-staining property, and initial roll-up performance; and in particular it is suitable for applications such as a presensitized plate for lithography and as a photoresist. Also, the composition of this invention is useful as a printing ink; an adhesive for metal foil, film, paper, and fabrics; and as a photocurable paint for metal, plastics, paper, wood, metal foil, fabrics, glass, paperboard, paperboard for box making, and for signs used in locations such as roads, parking lots, and airports, for example.

[0036]

When the invented composition is used, for example, as a vehicle of printing ink, it may be colored with previously known dyes, and at the same time colored with various organic pigments known in the art such as molybdate orange, titanium white, chromium yellow, phthalocyanine blue, and carbon black, for example. The quantity of the vehicle is from approximately 20% to 99.9% of the total weight of the composition, and the quantity of the coloring agent is in a range of approximately 0.1% to 80%. The materials that are printed may be paper, clay-coated paper, and paperboard for box making.

[0037]

In addition, the invented composition can be used as a vehicle of a printing ink for cloth of natural fiber or synthetic fiber, and as a vehicle for an agent to impart water repellency, oil resistance, soil resistance, and crease resistance to fabrics.

[0038]

In the case that the invented photopolymerizable composition is used as an adhesive, at least one of the adherends must be translucent to ultraviolet light or visible light. Typical examples of laminates obtained by lamination of a substrate using the invented composition include cellophane coated with polymer, for example cellophane coated with polypropylene, metals such as aluminum or copper coated with polyethylene terephthalate, and aluminum coated with polypropylene. /10

[0039]

The invented photopolymerizable composition can be used, in the form of coating material, for printing or coating the surfaces of glass or plastics by rolling or spraying. Coloration coating methods

may be used for glass, polyester film, vinyl polymer film, polymer-coated cellophane, as well as treated or untreated polyethylene and treated or untreated polypropylene for such things as disposable cups and bottles. Tinplate that has been sized, or that has not been sized, is included as an example of a metal that may also be coated.

[0040]

A photosensitive image-forming material prepared from the invented photo-curable photopolymerizable composition is a material that has a layer comprising the invented composition on the surface of a sheet-shaped or plate-shaped substrate as a photo-sensitive element.

[0041]

One mode of a photosensitive image-forming material that utilizes the invented composition is a structure wherein a film of the invented composition is formed on a the surface of a substrate, and a transparent plastic film is further formed thereon. A material having this structure may be used by pealing off the transparent plastic film immediately before an image exposure to be described below; alternatively an image may be exposed while the transparent plastic film is present, passing through the transparent plastic film, or passing through the support in a case where the support is transparent; subsequent peeling away of the transparent plastic film leaves the layer of the exposed and cured portion on the substrate, and the layer of the unexposed and uncured portion remains on the transparent plastic film (alternatively, the exposed and cured portions of the layer remain on the transparent plastic film, and the unexposed and uncured portions of the layer remain on the substrate); in other words, it is possible to use [the invented composition] to particular advantage as a material for the so-called peel-development mode.

[0042]

With regards to a sensitive image-forming material used in the invented composition, image exposure is accomplished by exposure to light of a predetermined portion of the photopolymerizable composition layer until an addition polymerization reaction occurring in the light-irradiated portion attains the desired thickness. The unexposed part of the layer of the composition is removed, for example by using a solvent that dissolves the ethylenic compound (monomer or prepolymer) but does not dissolve the polymer, or by so-called peel-off development. When used in a photosensitive image-duplicating material, the thickness after solvent removal (drying) should be in the range of 2 to 150 microns thick, preferably 3 to 100 microns thick. Flexibility decreases in inverse proportion to the thickness of the layer, and wear resistance decreases in proportion to the thinness of the layer.

[0043]

The photopolymerizable compositions of the invention can be used as printing ink, coating material, and adhesive without any volatile solvent. In these cases, they have many advantages over the conventional oil-containing resin type and solvent type inks and coating materials.

[0044]

The invented photopolymerizable composition has a faster photo-polymerization rate with the use of a photopolymerization initiator composed of easily obtained compounds. More specifically, it has the effect termed high sensitivity, and it is able to confer a photo-polymerization speed that is faster than polymerizable compounds in general that have ethylenic unsaturated double bonds in the photopolymerization initiator as described above; accordingly, it has a wide range of applications.

[0045]

The invention and its effect are described in more specifically below with reference to application examples and comparative examples.

[0046]

Application Examples 1-10 and Comparative Examples 1 and 2

(1) Manufacture of a photosensitive material

The composition of a photopolymerizable composition (solution) is given in Table 1. The numerals express parts by weight. A dash (-) indicates that [the listed ingredient] was not used.

[0047]

The ingredients of Table 1 were placed in a vessel and stirred for 3 hours and caused to be dissolved. The resulting solution was coated onto an aluminum plate by a spinner (rotational coating machine), and this was dried for 10 min at a temperature of 80°C, thus forming a photosensitive layer (layer of a photopolymerizable composition). The thickness of the photosensitive layer after drying was approximately 10 microns.

[0048]

(2) Measurement of the sensitivity of the photosensitive material

A photosensitive layer of photosensitive material was exposed to a light source (mercury vapor lamp, 2 kw) placed 50 cm away, for 15 sec, with an optical wedge (graduated into 0-15 steps) having an

optical filtration ratio of $\sqrt{2}$, depressurized and hermetically sealed, placed on the sensitive layer. The photosensitive layer was developed by treatment with 1,1,1-trichloroethane for 30 sec. The highest /11 step of the wedge corresponding to the manifested image was regarded as the sensitivity of the material. The higher the step, the higher the sensitivity.

[0049]

The following substances were used as the binder for the photopolymerizable composition.

[0050]

Polyethylene chloride: a 40 wt% toluene solution with a viscosity of approximately 90 cps at 25°C; a high molecular weight compound for which the chlorine content is approximately 66 wt%.

Methyl polymethacrylate: limiting viscosity at 30°C for methyl ethyl ketone solution.

[0051]

["] A high molecular weight compound for which 30°C methyl ethyl ketone is 0.282.

[0052]

In Table 1, E indicates the application examples and C indicates the comparative examples.

[0053]

TABLE 1. Composition of photopolymerizable compositions (solutions) (in parts by weight)

| | | | C1 | C2 | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 | E9 | E10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 6 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
| 2 | | 12 | – | – | 3 | – | – | – | – | – | – | – | – | – |
| | 7 | 13 | – | – | – | 3 | – | – | – | – | – | 1 | – | 3 |
| | | 14 | – | – | – | – | 3 | – | – | – | – | – | – | – |
| | | 15 | 3 | – | – | – | – | 3 | – | – | 3 | 2 | 3 | – |
| | | 16 | – | – | – | – | – | – | 3 | – | – | – | – | – |
| | | 17 | – | – | – | – | – | – | – | 3 | – | – | – | – |
| | 8 | 18 | – | 3 | 2 | 2 | 2 | 2 | 2 | 2 | – | 1 | 2 | – |
| | | 19 | – | – | – | – | – | – | – | – | 2 | 1 | – | 2 |
| 3 | | 9 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | 45 | – | – |
| | | 10 | – | – | – | – | – | – | – | – | – | – | 45 | 45 |
| 4 | | 11 | 500 | 500 | 500 | 500 | 500 | 500 | 500 | 500 | 500 | 500 | 500 | 500 |
| 5 | | | 2 | 0 | 4 | 7 | 3 | 14 | 8 | 6 | 13 | 11 | 12 | 7 |

Key: 1 Ethylenic compound

2 Photopolymerization initiator

3 Binder

4 Solvent

5 Sensitivity

6 Pentaerythritol trimethacrylate

7 Component (a)

8 Component (b)

9 Polyethylene chloride

10 Methyl polymethacrylate

11 1,2-dichloroethane

12 Xanthone

13 Fluorenone

14 Benzoin methyl ether

15 Benzanthrone

16 1,2-benzanthraquinone

17 Thioxanthone

18 1-benzyl-1,4-dihydronicotinamide

19 1-(4-ethylbenzyl)-1,4-dihydronicotinamide